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Annual Technical Report for Grant No. NAGW-661

Covering the period from December 1, 1985 to November 30, 1986

Measurement of HO$_2$ Chemical Kinetics with a New Detection Method

Submitted by:

Long C. Lee and Masako Suto
Department of Electrical & Computer Engineering
San Diego State University
San Diego, CA 92182
Tel. (619) 265-3701

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I. Introduction

This report describes the results obtained in the period from December 1, 1985 to November 30, 1986 for the research program currently supported by the NASA under Grant No. NAGW-661. In this program, the reaction rate constants of HO_2+O_3 were measured at various temperatures using a new developed HO_2 detection method. HO_2 was detected by the $OH(A-X)$ emission produced from photodissociative excitation of HO_2 at 147 nm. In order to examine the possible interference of other emitting species with the HO_2 detection, the photoexcitation processes of all the chemical species existing in the discharge-flow tube were also investigated in this program. The research results are summarized below.

II. Research Accomplished

A. Reaction Rate Constants of HO_2+O_3 at 280-365 K

The reaction rate constant of HO_2+O_3 at room temperature was measured for which the result was described in detail in a paper attached as Appendix A. The measurement was extended to other temperatures in the range of 280-365 K. The result is shown in Fig. 1. Our result is slightly lower than the recent measurement of Howard and Sinha (reported in the Proceedings of the CMA Sponsored Meeting on Stratospheric Chemistry), which is also shown in Fig. 1 for comparison. The reaction rate constants at the temperatures lower than 280 K and higher than 365 K will be measured in the next funding period.
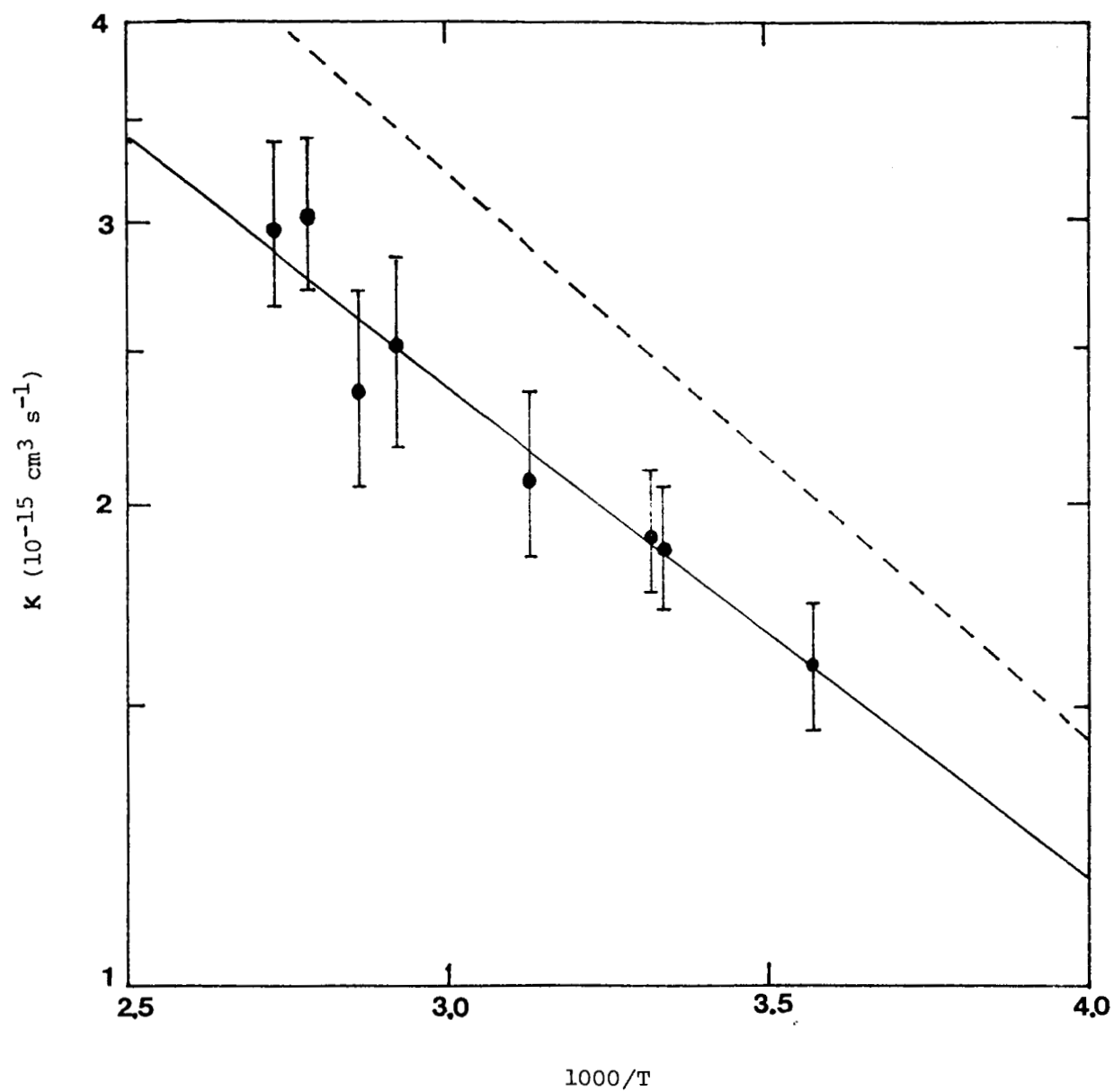
Fig. 1   The reaction rate constants of HO_2+O_3.   The dashed line represents the data of Howard and Sinha.

B. Emissions from VUV Excitation of Cl_2

Cl_2 was used in the experiment to produce Cl atom that reacted with CH_3OH and O_2 to form HO_2. The fluorescence from VUV excitation of Cl_2 may affect the current measurement of HO_2 concentration, thus, the information for the VUV excitation process of Cl_2 is needed. The fluorescence from VUV excitation of CL_2 was investigated using synchrotron radiation as a light source. Our current result shows that the fluorescence cross section of Cl_2 at 147 nm is so small that the interference is minimal. The result for the VUV excitation of Cl_2 is described in a paper attached as Appendix B.

C. Emissions from VUV Excitation of C_2F_3Cl

C_2F_3Cl was used in the experiment as an OH scavenger. The emission from photodissociative excitation of this molecule may affect the HO_2 detection. Therefore, the VUV excitation process of C_2F_3Cl was investigated and the result was described in detail in a paper attached as Appendix C which was accepted for publication in Chemical Physics.

C_2F_3Cl has a fluorescence cross section of 2.5×10^{-19} cm^2 at 147 nm, which is in the same order of magnitude as the fluorescence cross section of HO_2 of $(0.5 - 1) \times 10^{-19}$ cm^2., Thus, the fluorescence from C_2F_3Cl has a potential to interfere with the HO_2 detection. The fluorescence from C_2F_3Cl was dispersed to identify the emission systems to be $CF_2(\tilde{A}-\tilde{X})$ and $CFCl(\tilde{A}-\tilde{X})$ which are mainly in the 340-600 nm region. This fluorescence wavelength is longer than that of the OH(A-X) system of 306-330 nm. Using a band-pass filter that transmits 310 ± 10 nm, the

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fluorescence from C_2F_3Cl is essentially blocked, thus, its interference with the HO_2 detection is minimal.

Combining the current results of Cl_2 and C_2F_3Cl with our previous measurements on HCl, CH_3OH, CH_2O, O_3, and C_3H_8, it is conclusive that the detection of HO_2 by photofragment emission is not seriously disturbed by other emissions possibly produced by VUV excitation of other molecules in the flow tube. The applicability of the photofragment detection method to the rate measurement for the HO_2+O_3 reaction is thus established.

III. Cumulative Publications and Presentations

Our preliminary works have been reported in scientific community as listed below:

1. M. Suto and L. C. Lee, "Photofragment Emission from HO_2 and its Application to the HO_2 Kinetics Study", presented at the Informal Atmospheric Kinetics Meeting, Jet Propulsion Laboratory, Pasadena, CA, Jan. 18, 1985.

2. M. Suto, "Study of the HO_2+O_3 Reaction by Detecting HO_2 from Photofragment Emission", Seminar presented to the Naval Research Laboratory, Washington D. C., June 14, 1985.

3. L. C. Lee and M. Suto, "Photoexcitation Process of Cl_2 in VUV", presented at the 1985 SRC Users Group Meeting, Madison, Wisconsin, Oct. 21-22, 1985.

4. L. C. Lee, M. Suto and K. Y. Tang, "Quantitative VUV Spectroscopy of Cl_2", J. Chem. Phys. 84, 5277 (1986).

5. E. R. Manzanares, M. Suto, and L. C. Lee, "Measuring HO_2+O_3 Reaction Rate Constant by Detecting HO_2 from Photofragment Fluorescence", presented at the XVII Informal Conference on Photochemistry, Boulder, CO, June 22-26, 1986.

6. E. R. Manzanares, M. Suto, L. C. Lee, and D. Coffey, Jr., "Reaction Rate Constants of HO_2+O_3 Measured by Detecting HO_2 from Photofragment Fluorescence", J. Chem. Phys. 85, 5027 (1986).

7. J. B. Nee, X. Wang, M. Suto, and L. C. Lee, "CF_2 and CFCl Fluorescence from VUV Excitation of C_2F_3Cl", Chem. Phys. in press (1986).

IV. APPENDIX

A. "Reaction Rate Constant of HO_2+O_3 Measured by Detecting HO_2 from Photofragment Fluorescence"

B. "Quantitative VUV Spectroscopy of Cl_2"

C. "CF_2 and $CFCl$ Fluorescence from VUV Excitation of C_2F_3Cl"

CF_2 and CFCl Fluorescence from VUV Excitation of C_2F_3Cl

J. B. Nee [a)], Xiuyan Wang, Masako Suto and L. C. Lee [b)]
Department of Electrical and Computer Engineering
San Diego State University
San Diego, California 92182

ABSTRACT

The photoexcitation process of C_2F_3Cl molecule was investigated in the 106-230 nm region using synchrotron radiation as a light source. Photoabsorption and fluorescence cross sections were measured and used to determine the fluorescence quantum yield. Fluorescence yield starts to appear at 170 nm and increases to about 2% at 155 nm. The fluorescence spectra were dispersed to identify the emitting species. At the excitation wavelength of 155 nm, the emission system is CFCl $(\tilde{A}-\tilde{X})$, and at 123.9 nm, both the $CF_2(\tilde{A}-\tilde{X})$ and CFCl $(\tilde{A}-\tilde{X})$ systems are observed. The dissociation processes that produced these excited species are discussed.

a) Present address: Dept. of Physics, National Central University, Taiwan 32

b) also, Department of Chemistry, San Diego State University

I. INTRODUCTION

In a recent study of reaction kinetics of $HO_2 + O_3$ by detecting HO_2 with photofragment emission in our laboratory, emission from excitation of C_2F_3Cl at 147 nm was observed when it was introduced into the system as a scavenger for the OH radical [1]. This motivated us to investigate the photochemistry of C_2F_3Cl in vacuum ultraviolet (VUV) region in order to understand the nature of the UV emission. The VUV absorption spectrum of C_2F_3Cl is itself of interest in understanding the Rydberg states of chlorofluoroethylenes, which show an absorption character similar to that of ethylene. The photoexcitation process of C_2F_3Cl is also interesting for the possible role it plays in atmospheric chemistry, because it is a member of halocarbons and releases F and Cl atoms into the atmosphere by solar radiation.

Photoexcitation of C_2F_3Cl may produce excited dihalogen carbene radicals of CF_2 and CFCl which are known to have strong transitions in the ultraviolet (UV) region. These radicals can be generated from $F_2C=CFCl$ by chemical reaction with oxygen atoms [2,3], UV photolysis [4-6], and infrared multiphoton dissociation [7]. The UV emission system of $CF_2(\tilde{A}^1B_1-\tilde{X}^1A_1)$ has been extensively investigated [8,9]; but, the CFCl $(\tilde{A}^1A''-\tilde{X}^1A')$ system has been studied only recently [7,10]. Up-to-date information regarding the photoabsorption process of C_2F_3Cl has been summarized in a recent book by Robin [11].

II. EXPERIMENTAL

The synchrotron radiation experiment was carried out in the electron storage ring at the University of Wisconsin. Experimental details have been described in a previous publication [12]. Synchrotron radiation was dispersed by a 1-m vacuum monochromator before entering a gas cell. UV fluorescence was detected in the direction perpendicular to the light beam by an EMI (9558QB) photomultiplier tube (PMT). Light source intensity was measured by another PMT attached to the end of the gas cell. The VUV light source was converted to UV light by sodium salicylate coated outside a LiF window. The optical path length for absorption measurement was 39.1 cm. C_2F_3Cl was supplied by Matheson with a purity better than 99.0%; no further purification was made.

The apparatus for dispersing the fluorescence spectrum has been described previously [13]. A pulsed discharge lamp associated with a 1-m vacuum monochromator (McPherson 225) was used as the light source. Fluorescence was dispersed by a 0.3-m monochromator (McPherson 218) and detected by a PMT (EMI 9558QB). Atomic emission lines of CIV at 155 nm and NV at 123.9 nm were used to excite C_2F_3Cl. A gated photon counting system was used to process the fluorescence signal.

III. RESULTS

The photoabsorption cross section of C_2F_3Cl at 106-225 nm was measured. The absorbance $\ln(I_o/I)$ was linearly dependent on C_2F_3Cl pressure up to 100 mtorr at 105-180 nm. In the 180-230 nm

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region, C_2F_3Cl gas up to 10 torr was used because of weak absorption. The absorption spectrum obtained at a resolution of 0.2 nm is shown in Figure 1, curve a. Experimental uncertainty for the absorption cross section is estimated to be within 10% of the given value. Positions of the V - N transition [14] and the Rydberg series assigned by Scott and Russel [15] are also indicated in Figure 1.

The total fluorescence cross section measured simultaneously with the absorption cross section is shown in Figure 1, curve b. The fluorescence cross section was calibrated against the fluorescence of OH(A-X) from VUV photodissociation of H_2O for which fluorescence cross section has been measured [12]. The PMT response was nearly constant in the 185-400 nm region and decreased at the longer wavelength. Since the fluorescence is essentially in the UV region, the PMT response was not corrected in the fluorescence cross section measurement.

The fluorescence quantum yield was determined as a ratio of the fluorescence cross section to the absorption cross section. The fluorescence quantum yield in the 106-170 nm region is shown in Figure 2. Experimental uncertainty for the fluorescence cross section is estimated to be within 30% of the given value.

Fluorescence spectra from the photodissociation of C_2F_3Cl by atomic lines from a discharge lamp are shown in Figures 3 and 4. Figure 3a shows the dispersed emission spectrum excited at 155 nm; Figure 3b shows the spectrum when 1 atm of Ar was added for the vibrational relaxation of excited species. When the

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vibrational energy was relaxed, the emission shifted to red. This spectrum is identified as the CFCl ($\tilde{A}-\tilde{X}$) system by comparing it with the laser-induced-fluorescence spectrum [7]. The radiative lifetime of CFCl($\tilde{A}-\tilde{X}$) is 700 $\pm$ 10 ns [7]. Thus, at low gas pressure, the quenching of the emission by parent molecule is negligible.

The emission spectrum produced by photoexcitation of C_2F_3Cl at 123.9 nm is shown in Figure 4. The long wavelength section of this spectrum is similar to Figure 3a, but at wavelengths shorter than 350nm, the emission is mainly due to the $CF_2(\tilde{A}-\tilde{X})$ system [8,9]. These emitting species may not be simultaneously produced by a single photodissociation process such as, $C_2F_3Cl \rightarrow CF_2^*+CFCl^*$, because this requires energy higher than 10 eV. The photodissociative excitation of C_2F_3Cl will be discussed later.

IV. DISCUSSION

A. Photoabsorption Spectrum
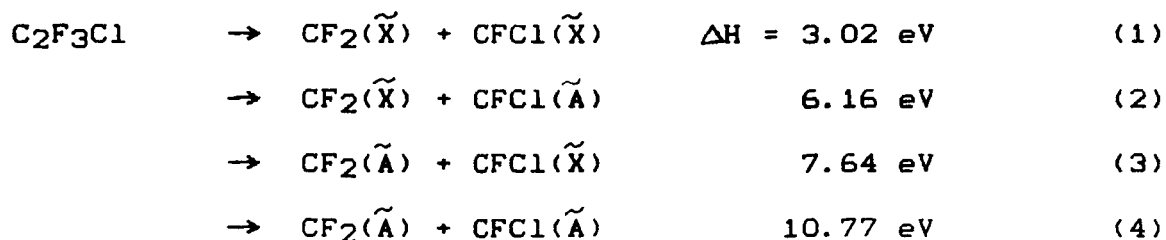
C_2F_3Cl, like other chlorofluoroethylenes, has an absorption spectrum quite similar to that of ethylene [11]. The electronic transition of an electron excited from the π orbital of the C=C bond (the ground state, N) to the π^* orbital forms a triplet state, T, and a singlet state, V. The electron may also be excited to Rydberg states, R. The absorption spectra of ethylene-type molecules have been extensively investigated in the VUV region. The VUV excitation process is primarily due to the V and R $\leftarrow$ N transitions; however, the vibronic structures for these molecules have not yet been thoroughly studied [11].

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Scott and Russel [15] have assigned two Rydberg states for C_2F_3Cl among other chlorofluoroethylenes. The Rydberg series converging to the first ionization limit are shown in Figure 1. Using photoelectron spectroscopy, Lake and Thompson [16] determined the vertical ionization potential (transition of maximum probability) of C_2F_3Cl to be 10.24 eV (121.1 nm), and adiabatic ionization potential (transition to v'=0 of the upper state) to be 9.84 eV (126 nm). The excited states of C_2F_3Cl have been compared with those of other halogenated-ethylenes by electron-impact spectroscopy [17, 18]. The broad continuum extending from about 140 nm to 225 nm is assigned to the V - N transition overlapped with Rydberg states [15]. This continuum is superimposed with the vibrational structure of the C=C stretching mode.

B. Fluorescences of CF_2 and CFCl.

Energy thresholds for the photodissociative excitation process of C_2F_3Cl can be determined from the following heats of formation: ΔH_f^0 = -120.8 $\pm$ 1.1 kcal/mol for C_2F_3Cl [19], -49 $\pm$ 3 kcal/mol for CF_2[20], and -2 $\pm$ 7 kcal/mol for CFCl [20]. The electronic energies for $CF_2(\tilde{A}^1B_1)$ and CFCl $(\tilde{A}^1A")$ are 4.616 [8] and 3.135 eV [7], respectively. The energies required for various processes are as follows:

$$C_2F_3Cl \rightarrow CF_2(\tilde{X}) + CFCl(\tilde{X}) \qquad \Delta H = 3.02 \text{ eV} \qquad (1)$$

$$\rightarrow CF_2(\tilde{X}) + CFCl(\tilde{A}) \qquad 6.16 \text{ eV} \qquad (2)$$

$$\rightarrow CF_2(\tilde{A}) + CFCl(\tilde{X}) \qquad 7.64 \text{ eV} \qquad (3)$$

$$\rightarrow CF_2(\tilde{A}) + CFCl(\tilde{A}) \qquad 10.77 \text{ eV} \qquad (4)$$

The other radicals such as C_2F_3 or C_2F_2Cl may not emit strongly, because the fluorescence spectra shown in Figures 3 and 4 are mainly from CF_2 and $CFCl$.

The spectrum of quantum yield shows two broad peaks around 123 nm and 155 nm. Since the excitation of C_2F_3Cl at 155 nm produces $CFCl(\tilde{A})$ only, the quantum yield in the 135-170 nm region is presumably due to $CFCl(\tilde{A})$ only, while the second peak at 123 nm probably indicates the existence of a state producing $CF_2(\tilde{A})$. As shown in Figure 2, the threshold wavelength for the production of $CFCl(\tilde{A})$ is at 170 nm (7.29 eV), and it is likely around 135 nm (9.18 eV) for $CF_2(\tilde{A})$. These fluorescence thresholds are much higher than the thermochemical thresholds of processes (2) and (3). Thus, the vertical energies of the dissociative states that produce $CF_2(\tilde{A})$ and $CFCl(\tilde{A})$ are higher than the dissociation thresholds.

The fluorescence quantum yield is determined from the transition probability for excitation to a repulsive state (direct dissociation) or the interaction strength between a discrete state and a dissociative state (predissociation). Since the fluorescence quantum yields for both the vibrational bands and the absorption continuum in the 140-170 nm region are about the same, the strength for producing the CFCl(A) by either direct photodissociation process or predissociation process is about the same. The peak for the spectrum of fluorescence yield can be used to determine the vertical energy of the dissociative state which is about 8.0 eV for $CFCl(\tilde{A})$ and about 10 eV for $CF_2(\tilde{A})$.

For the 10 eV band, the peak wavelength of quantum yield may be affected by the onset of ionization process. In general, the fluorescence quantum yield decreases at wavelengths shorter than ionization limit.

The shift of the CFCl emission spectrum to red when Ar is added as shown in Figures 3a and 3b indicates that $CFCl(\tilde{A})$ is vibrationally excited. Based on the threshold energy of process (2), an excess energy of 1.84 eV is available. This excess energy is enough to excite the molecule into high vibrational quantum numbers which can be calculated from the spectroscopic data (6,9). However, the vibrational spectrum shown in Figure 3 is very complicated, it is difficult to assign vibrational levels.

V. CONCLUSION

The photoabsorption and fluorescence cross sections of C_2F_3Cl have been measured in the 106-230 nm region. Fluorescence spectra have been dispersed and identified to be the $CF_2(\tilde{A}^1B_1-\tilde{X}^1A_1)$ and $CFCl(\tilde{A}^1A''-\tilde{X}^1A')$ systems. The spectrum of fluorescence quantum yield shows two dissociative states. The threshold wavelengths for producing $CFCl(\tilde{A})$ and $CF_2(\tilde{A})$ were determined to be 170 and 135 nm, respectively.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1.   Photoabsorption and fluorescence cross sections of C_2F_3Cl in the 106-230 nm region in units of $Mb(10^{-18} cm^2)$. The wavelength positions of the $V \leftarrow N$ transition and the Rydberg series assigned by Scott and Russel are indicated.

Fig. 2.   Fluorescence quantum yield in the 106-175 nm region. The dashed line represents an average value.

Fig. 3.   Fluorescence spectra produced by photoexcitation of C_2F_3Cl at 155 nm. (a) Pure C_2F_3Cl of 80 mtorr and (b) 1 atmosphere Ar was added to (a). The monochromator resolution was 4 nm. The fluorescence spectrum is identified to be the $CFCl(\tilde{A}-\tilde{X})$ system.

Fig. 4.   Fluorescence spectrum produced by photoexcitation of 80 mtorr C_2F_3Cl at 123.9 nm. The monochromator resolution was 4 nm.
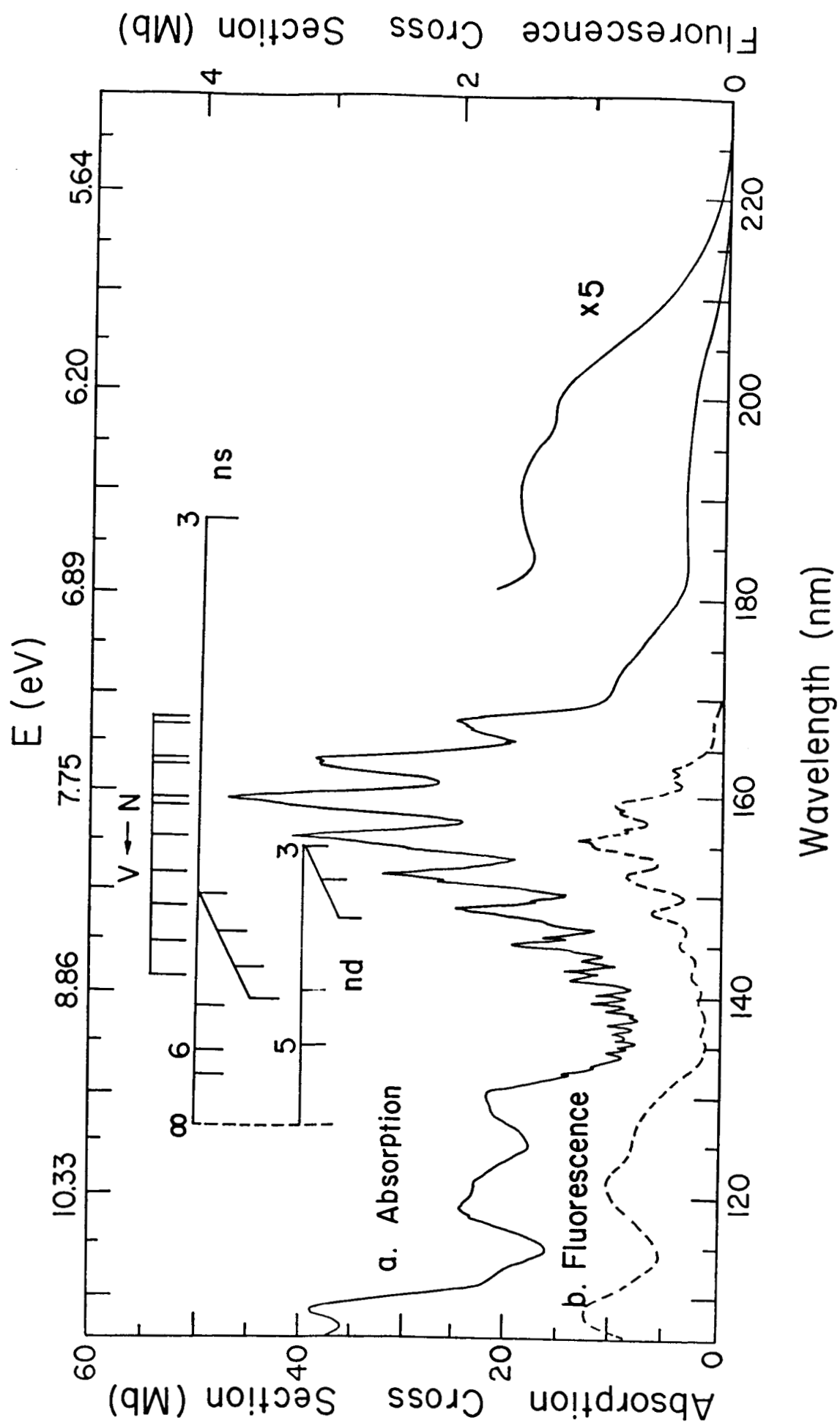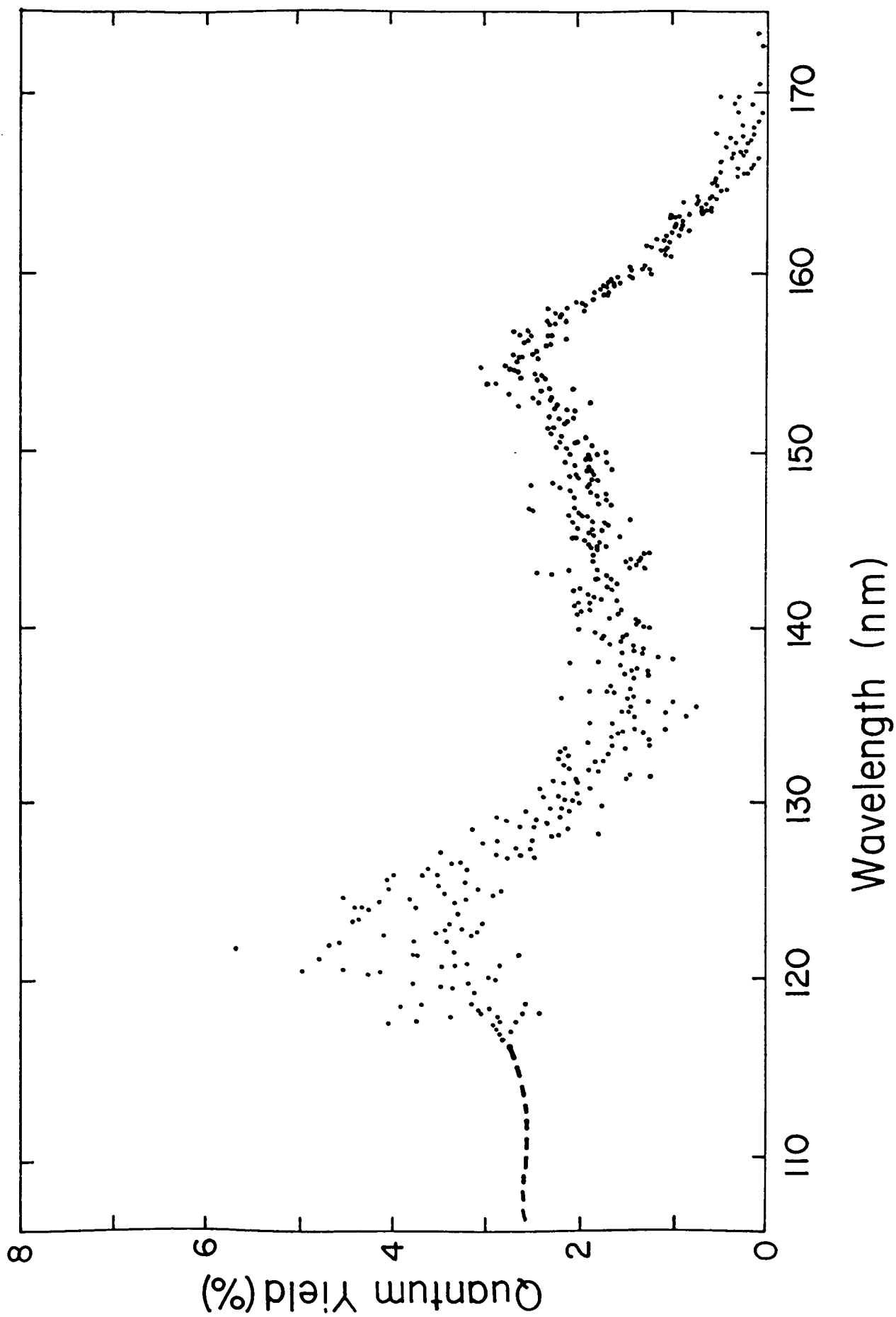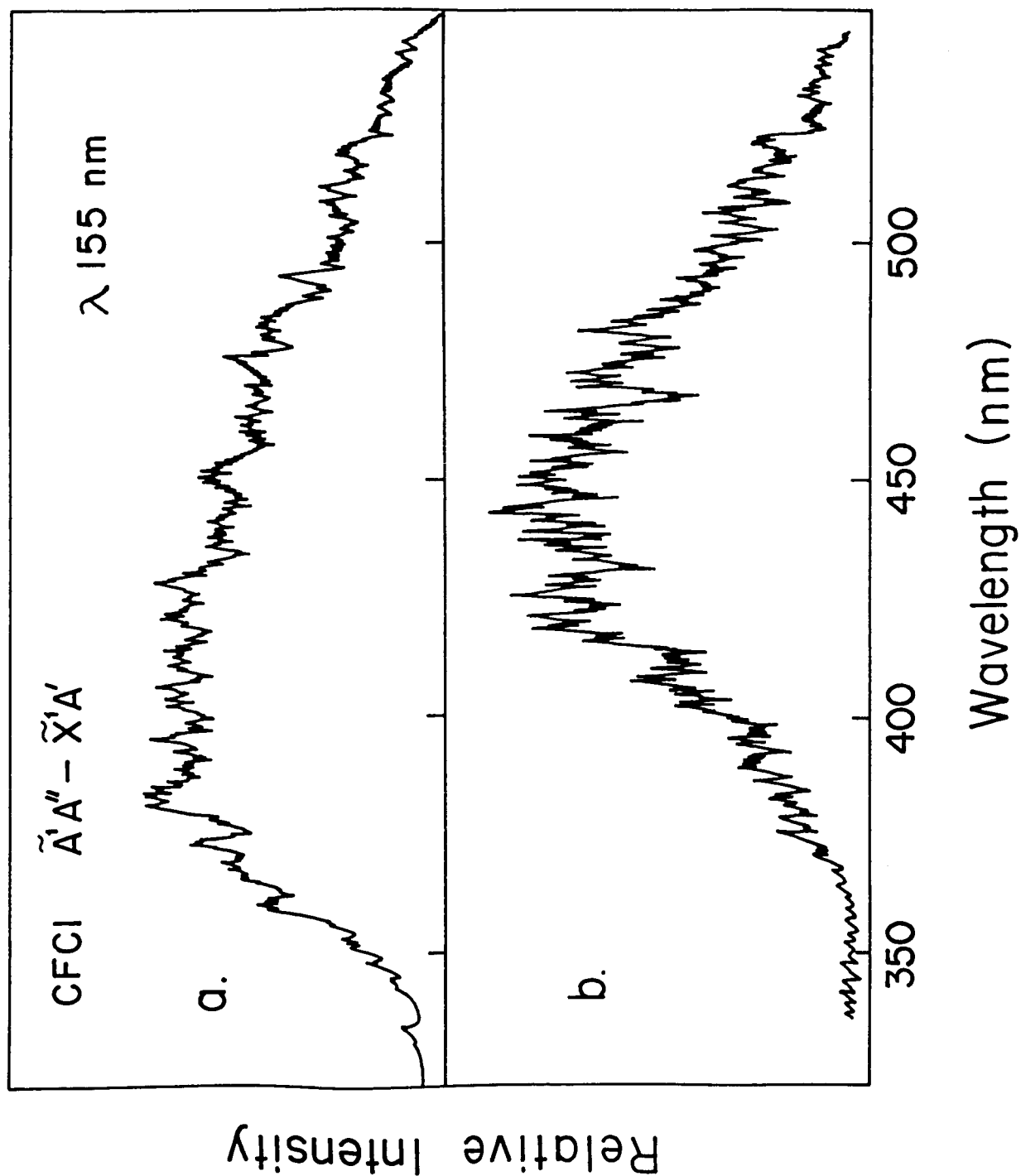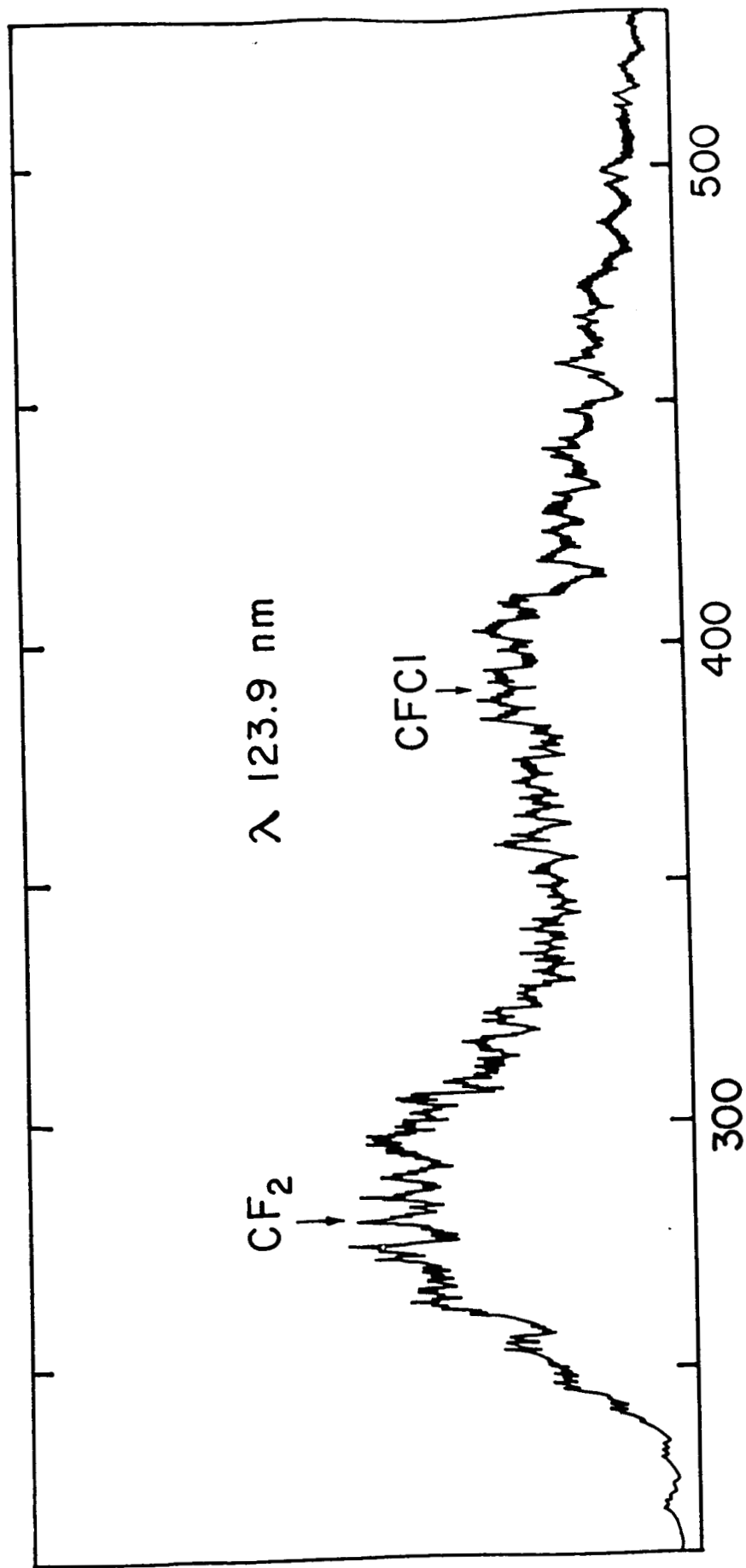
Fig. 1

Fig. 2

CFCl $\tilde{A}^1A'' - \tilde{X}^1A'$

λ 155 nm

a.

b.

Relative Intensity

Wavelength (nm)

350   400   450   500

Fig. 3

λ 123.9 nm

CF₂

CFCl

Wavelength (nm)

Relative Intensity

Fig. 4